

NASA TECHNICAL MEMORANDUM

NASA TM X- 64639

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THE EFFECT OF AMBIENT PRESSURE ON THE EVAPORATION RATE OF MATERIALS

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January 7, 1972

NASA

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1. REPORT NO. NASA TMX 64639	2. GOVERNMENT ACCESSION NO.	3. RECIPIENT'S CATALOG NO.	
4. TITLE AND SUBTITLE The Effect of Ambient Pressure on the Evaporation Rate of Materials		5. REPORT DATE January 7, 1972	
		6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) R. J. Naumann and W. M. Russell		8. PERFORMING ORGANIZATION REPORT #	
9. PERFORMING ORGANIZATION NAME AND ADDRESS George C. Marshall Space Flight Center Marshall Space Flight Center, Alabama 35812		10. WORK UNIT NO.	
		11. CONTRACT OR GRANT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS National Aeronautics and Space Administration Washington, D.C. 20546		13. TYPE OF REPORT & PERIOD COVERED Technical Memorandum	
		14. SPONSORING AGENCY CODE	
15. SUPPLEMENTARY NOTES Prepared by Space Sciences Laboratory, Science and Engineering			
16. ABSTRACT A simple expression is obtained using a diffusion model for the effect of ambient pressure on the outgassing or evaporation rate of materials. The correctness of the expression is demonstrated by comparing the estimates from this expression with actual weight loss measurements. It is shown that the rate of mass loss is governed by the ratio of mean free path to the characteristic dimension of the surface in question.			
17. KEY WORDS		18. DISTRIBUTION STATEMENT Unclassified — Unlimited	
19. SECURITY CLASSIF. (of this report) Unclassified	20. SECURITY CLASSIF. (of this page) Unclassified	21. NO. OF PAGES 18	22. PRICE \$3.00

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THE EFFECT OF AMBIENT PRESSURE ON THE EVAPORATION RATE OF MATERIALS

INTRODUCTION

It is well known that materials outgas when placed in vacuum. Initially, this outgassing rate may be high, particularly if the material contains absorbed impurities or if the material is an incompletely cured elastomer, adhesive, or paint. After a number of hours, depending on the material, a steady-state mass loss will result which is the evaporation of the material in question resulting from the atoms on the surface receiving sufficient energy from the tail of the Boltzman distribution to overcome the binding energy or the heat of vaporization.

In a high vacuum, the actual steady-state mass loss will simply be this evaporation rate. However, increasing the pressure will greatly inhibit the mass loss because evaporated molecules are retained in the vicinity of the parent surface by the presence of ambient molecules, thus increasing the probability of their being reabsorbed.

The objective of this study is to develop an expression for the mass loss as a function of ambient pressure of a material from diffusion theory and to compare the result with actual evaporation measurements.

THEORY

Consider a sphere of material with radius r_o . Molecules will leave the surface at the rate

$$N_{\text{evap}} = \sigma \nu_o e^{-E_o/kT} \quad (1)$$

where σ is the surface density (number of molecules per unit area), ν_o is the vibrational frequency, and the exponential term is the probability per vibrational cycle that a molecule with binding energy E_o will experience a fluctuation sufficient for it to escape the surface.

Let $n(r)$ be the number density of evaporated molecules at radius r . The rate at which molecules return to the surface per unit area is given by

$$\dot{N}_{\text{return}} = \frac{n\bar{v}}{4} \quad (2)$$

where \bar{v} is the average molecular speed given by

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} \quad (3)$$

where m is the mass of the molecule.

If the sphere of material were located in a closed container and allowed to come to equilibrium, eventually $\dot{N}_{\text{evap}} = \dot{N}_{\text{return}}$ and the number density would be given by

$$n = \sqrt{\frac{2\pi m}{kT}} \sigma \nu_o e^{-E_o/kT} \quad (4)$$

from which the vapor pressure can be obtained from the ideal gas law $P = nkT$,

$$P_{\text{vap}} = \sqrt{2\pi m kT} \sigma \nu_o e^{-E_o/kT} \quad (5)$$

Before equilibrium is reached, more material is evaporated than returns, resulting in a net material loss given by

$$\dot{N}_{\text{loss}} = \dot{N}_{\text{evap}} - \dot{N}_{\text{ret}} \quad (6)$$

In the presence of an ambient atmosphere, the loss rate is governed by the diffusion equation

$$J = -\mu k T \frac{dn}{dr} \quad (7)$$

where J is the diffusion current and μ is the mobility of the evaporated molecules in the ambient atmosphere, which by definition is

$$\mu = \frac{\lambda}{m \bar{v}} \quad (8)$$

where λ is the mean free path of the evaporated molecule in the ambient atmosphere.

In a free spherical expansion, the continuity equation requires $\nabla \cdot J = 0$, or

$$\frac{1}{r^2} \frac{d}{dr} (r^2 J) = 0 \quad (9)$$

or

$$\frac{dJ}{J} + \frac{2dr}{r} = 0 \quad (10)$$

from which

$$\ln J = -2 \ln r + C \quad (11)$$

or

$$J = C r^{-2} \quad (12)$$

From equation (7)

$$\frac{dn}{dr} = \frac{-C}{\mu k T r^2} \quad (13)$$

Integrating,

$$n = \frac{C}{\mu k T r} + D \quad (14)$$

where C and D are integration constants. With the condition that $n \rightarrow 0$ and $r \rightarrow \infty$, $D = 0$.

The constant C can be eliminated by combining equations (13) and (14), giving

$$\frac{dn}{dr} = -\frac{n}{r} \quad (15)$$

The current J then becomes

$$J = \frac{\mu n k T}{r} \quad (16)$$

Solving equation (16) for n and using the condition that $\dot{N}_{\text{loss}} = J$ at $r = r_o$, equations (2) and (6) yield

$$\dot{N}_{\text{loss}} = \dot{N}_{\text{evap}} - \frac{\bar{v}}{4} \frac{r_o \dot{N}_{\text{loss}}}{\mu k T} \quad (17)$$

or

$$\dot{N}_{\text{loss}} = \frac{\dot{N}_{\text{evap}}}{1 + \frac{\bar{v} r_0}{4 \mu k T}} \quad (18)$$

Using equation (8), \dot{N}_{loss} becomes

$$\dot{N}_{\text{loss}} = \frac{\dot{N}_{\text{evap}}}{1 + \frac{m \bar{v}^2 r_0}{4 \lambda k T}} \quad (19)$$

which using equation (3) becomes

$$\dot{N}_{\text{loss}} = \frac{\dot{N}_{\text{evap}}}{1 + \frac{2 r_0}{\pi \lambda}} \quad (20)$$

At ambient pressure, the mean free path is on the order of tenths of microns. If the source dimensions are on the order of centimeters, the actual transport away from the source is approximately 10^{-5} less than the evaporation rate. This transport will increase linearly with decreasing pressure until the mean free path is approximately equal to the source dimension, which corresponds to pressures of $10^{-5} - 10^{-6}$ atmospheres. At this point, practically every molecule evaporating diffuses away from the source; therefore, further decrease in pressure will have little effect in the loss rate.

EXPERIMENTAL RESULTS

Experimental measurements of evaporation of resorcinol ($\text{C}_6\text{H}_6\text{O}_2$) at varying pressures were made with a quartz crystal microbalance. A drop of approximately $0.2 \mu\text{l}$ of a resorcinol solution in ethanol was deposited on the

sensing crystal. The concentration was $0.01 \text{ mg}/\mu\ell$; therefore, the residue of resorcinol was approximately $2 \mu\text{g}$. At pressures less than 1 Torr, evaporation took place in minutes, whereas 10 or more hours were required at 1 atm.

The theoretical response of the quartz crystal microbalance is given by [1, 2]

$$\Delta F = \frac{\Delta m F^2}{k \rho A} \quad (21)$$

where k is a constant related to the elastic constants of quartz with a value of $1.66 \times 10^5 \text{ Hz cm}$.

The fundamental frequency F is 10^7 Hz and the sensitive area is 0.2 cm^2 . Taking $\rho = 2.6 \text{ gm/cm}^3$, then

$$\frac{\Delta F}{\Delta m} = 1.158 \times 10^9 \quad \text{Hz/gm} \quad (22)$$

It is well known that a quartz oscillator does not respond to a liquid in the same manner as to a solid. This is a result of the fact that the mass deposited on the surface must be vibrated as part of the crystal in order to be measured. In a liquid, only the viscous forces couple the liquid to the crystal, with the result that only the first few molecular layers are sensed. Another effect of a liquid is the dissipation of energy which lowers the amplitude of the output waveform. If the liquid on the crystal is sufficient, the oscillator will become critically damped and will cease operation.

One of the difficulties in using a rather volatile solid, such as resorcinol, in a liquid vehicle is that some of the solid will evaporate before complete solidification occurs. Therefore, one cannot observe the frequency shift corresponding to original mass of the solid. This can be seen examining the frequency shift during the test (Fig. 1) at atmospheric pressure. In this case, the evaporation rate did not reach a steady-state value for almost 2 hours. Extrapolating back to the beginning of the test, a total shift of 2212 Hz was observed which corresponds to $1.91 \times 10^{-6} \text{ gm}$ initial mass. The drop of ethanol/resorcinol deposited on the crystal spreads to approximately 3 mm in diameter, corresponding to an area of 0.0071 cm^2 . Using this and the theoretical sensitivity, the steady-state evaporation rate observed to be 460 Hz/hr corresponds to $1.56 \times 10^{-9} \text{ gm/cm}^2/\text{sec}$.

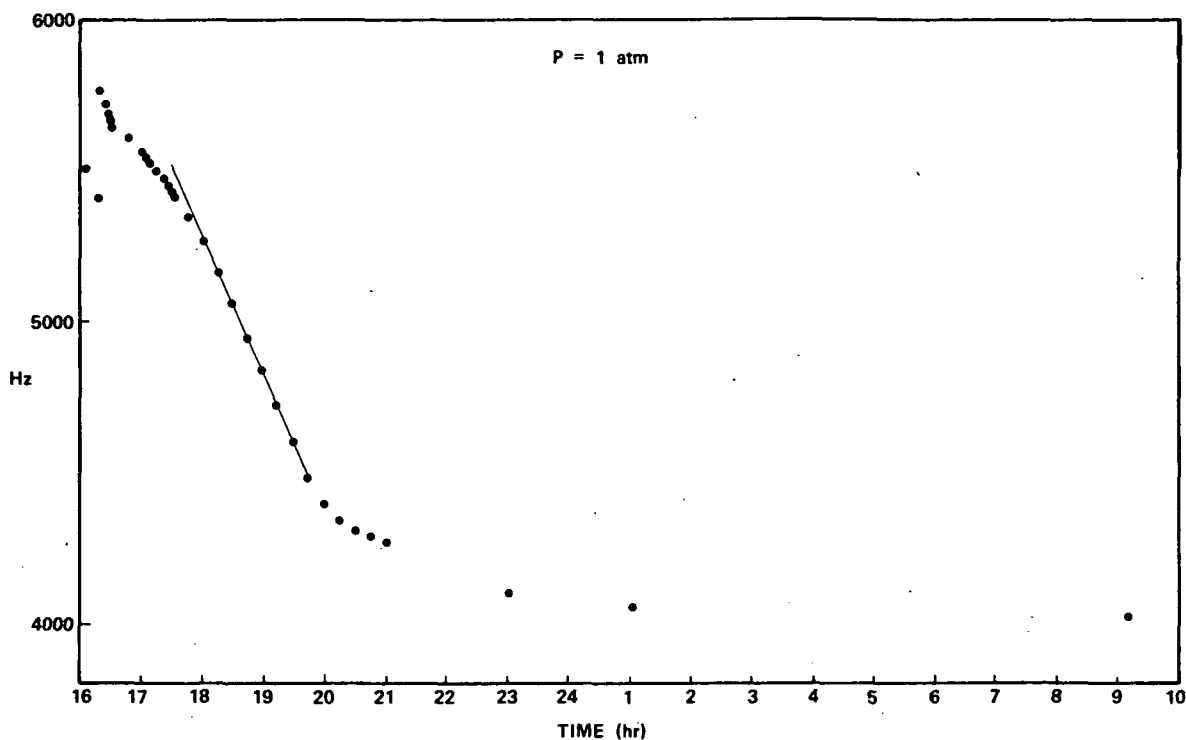


Figure 1. Evaporation curve for resorcinol at ambient pressure.

As the frequency falls to approximately 300 Hz above the background, the evaporation rate diminishes. There are two possible reasons for this: (1) the surface area probably diminishes as the material evaporates and (2) the residual resorcinol contamination in the chamber has also vaporized and increased the partial pressure in the entire chamber which reduces the diffusion rate away from the crystal. A very similar effect is observed, however, with the crystal outside the chamber and even when air is blown across the crystal, which more than doubles the evaporation rate. Since in this case there is certainly no increase in partial pressure of resorcinol near the crystal, it is concluded that this tail-off in the evaporation rate is primarily caused by a change in area.

Figures 2, 3, and 4 show the effect of $1/2$, $1/4$, and $1/760$ atm on the evaporation rate. Note that at $1/760$ the material has completely evaporated before the intended pressure was reached, which makes it impossible to obtain a measurement of evaporation rate at this pressure with the system used.

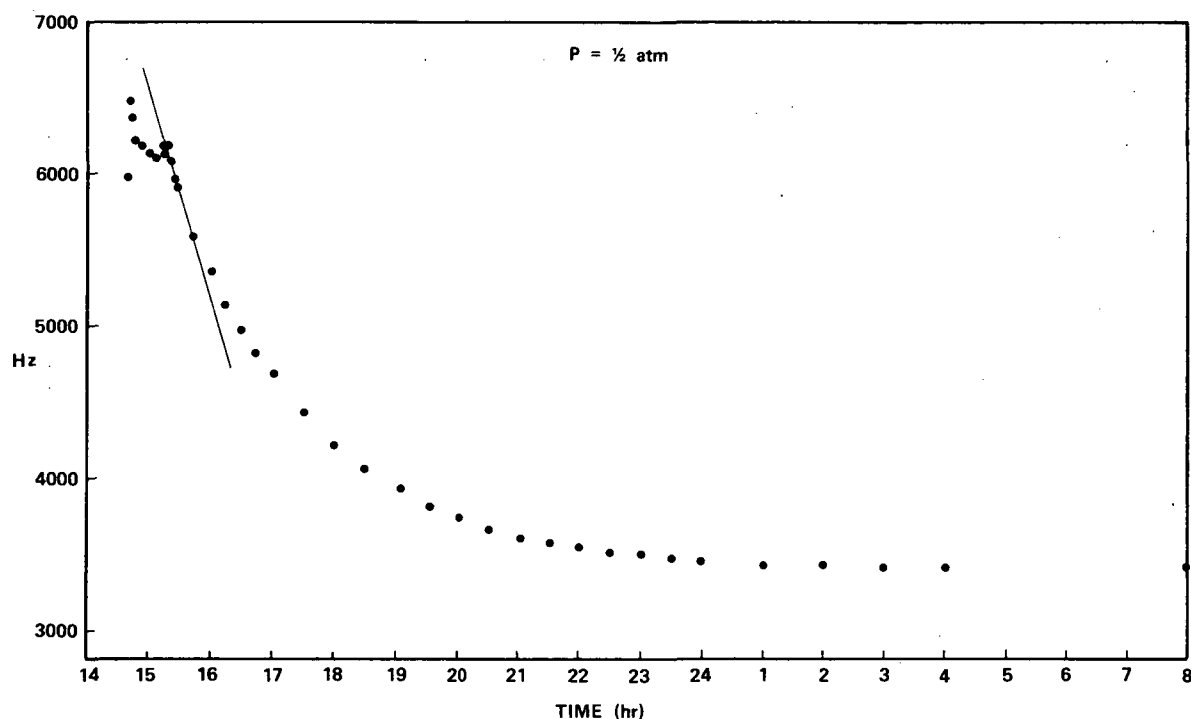


Figure 2. Evaporation curve for resorcinal at 1/2 atmospheric pressure.

The results are summarized in Figure 5 and compared with the theoretical results. Good comparison is found despite the approximations made in the computations and the difficulty in obtaining accurate measurements of evaporation rates.

COMPUTATION OF EVAPORATION RATES

To compute the evaporation rate of the resorcinal, \dot{N}_{evap} , r_o , and λ must be specified in order to use equation (20).

Combining equations (1) and (5), the \dot{N}_{evap} can be found:

$$\dot{N}_{\text{evap}} = \frac{P_{\text{vap}}}{\sqrt{2 \pi m k T}} \quad (23)$$

which is the Knudsen-Langmuir equation.

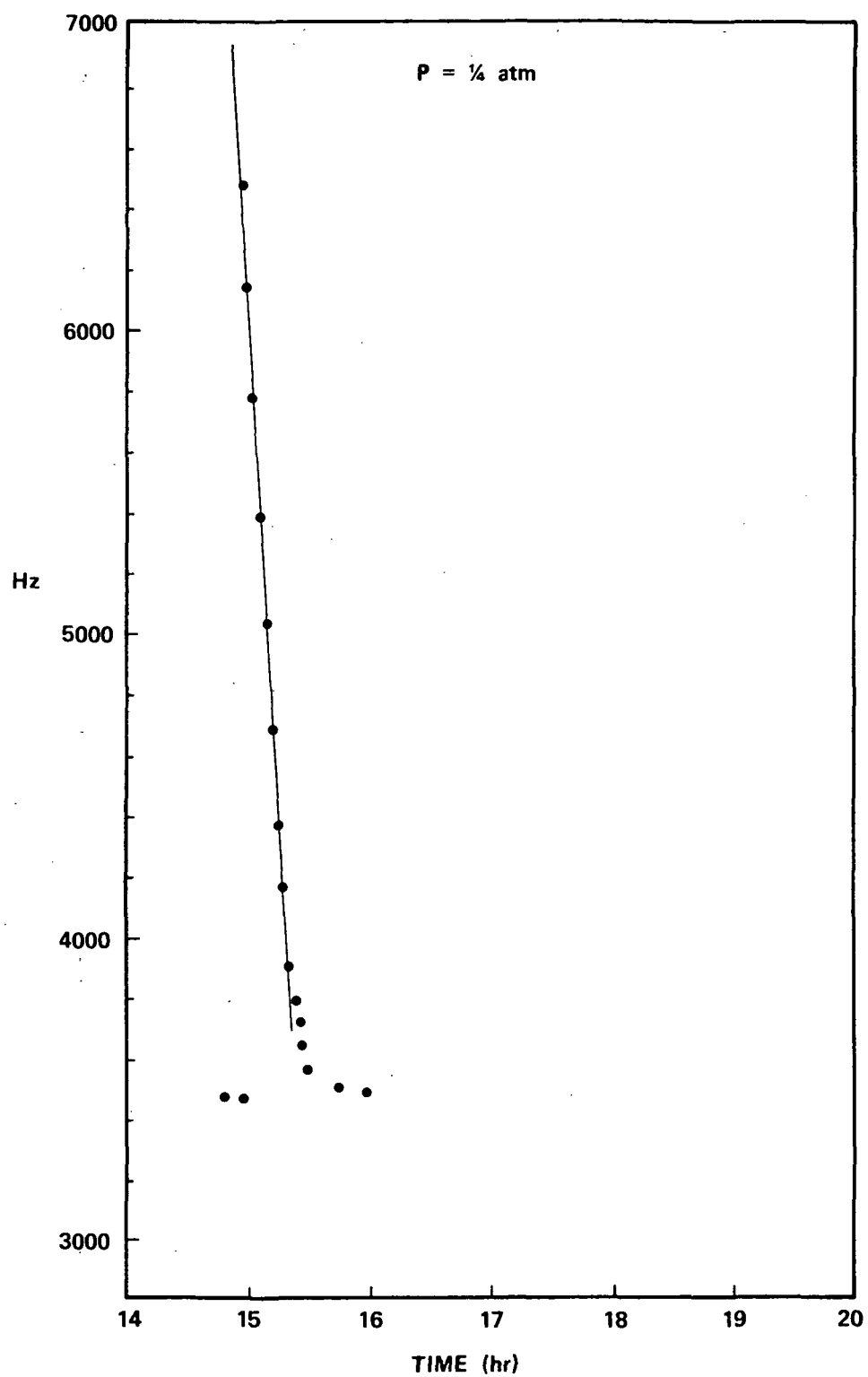


Figure 3. Evaporation curve for resorcinal at $\frac{1}{4}$ atmospheric pressure.

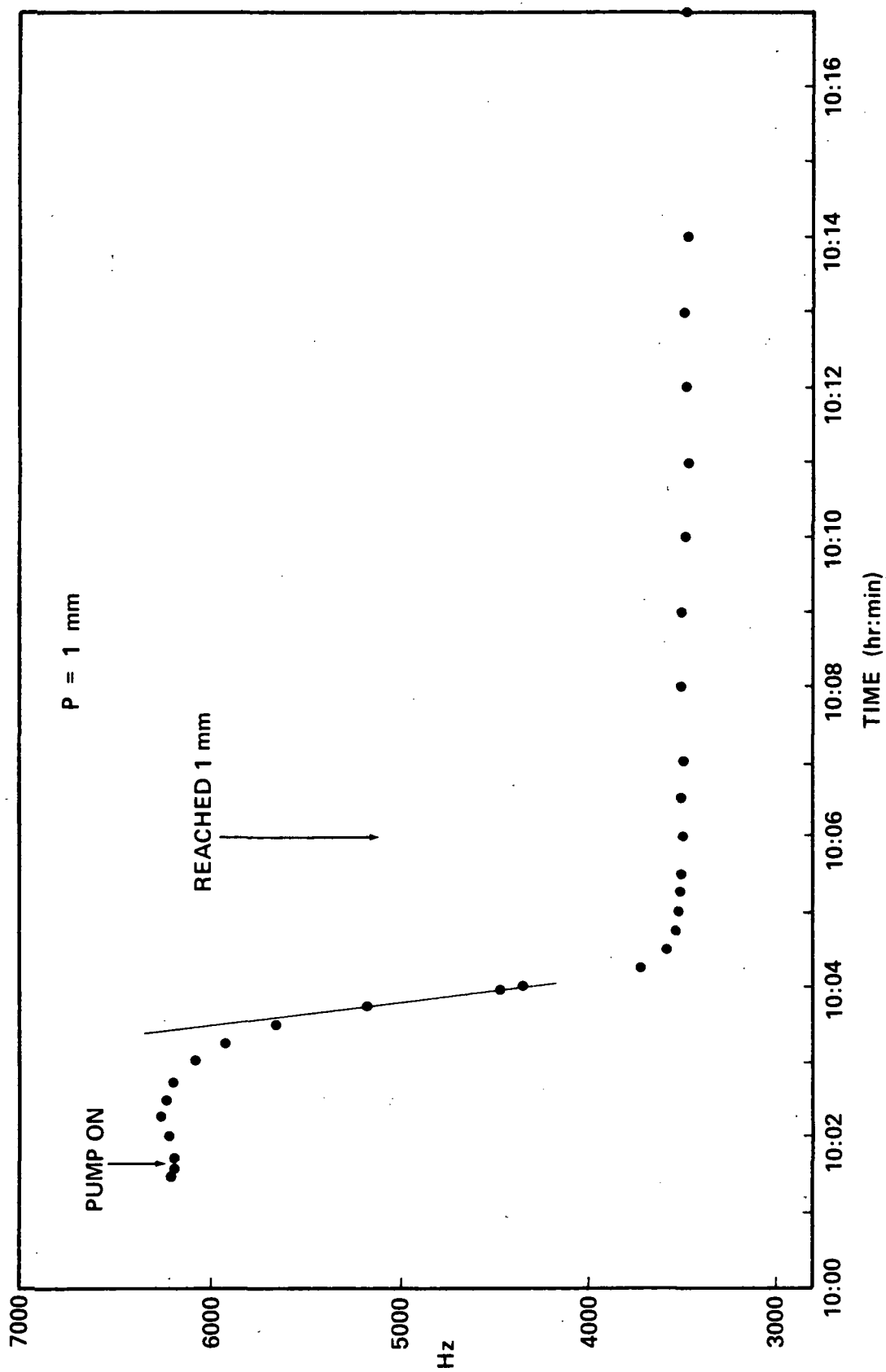


Figure 4. Evaporation curve for resorcinol at a pressure of 1 mm Hg.
(The sample completely evaporated before reaching 1 mm.)

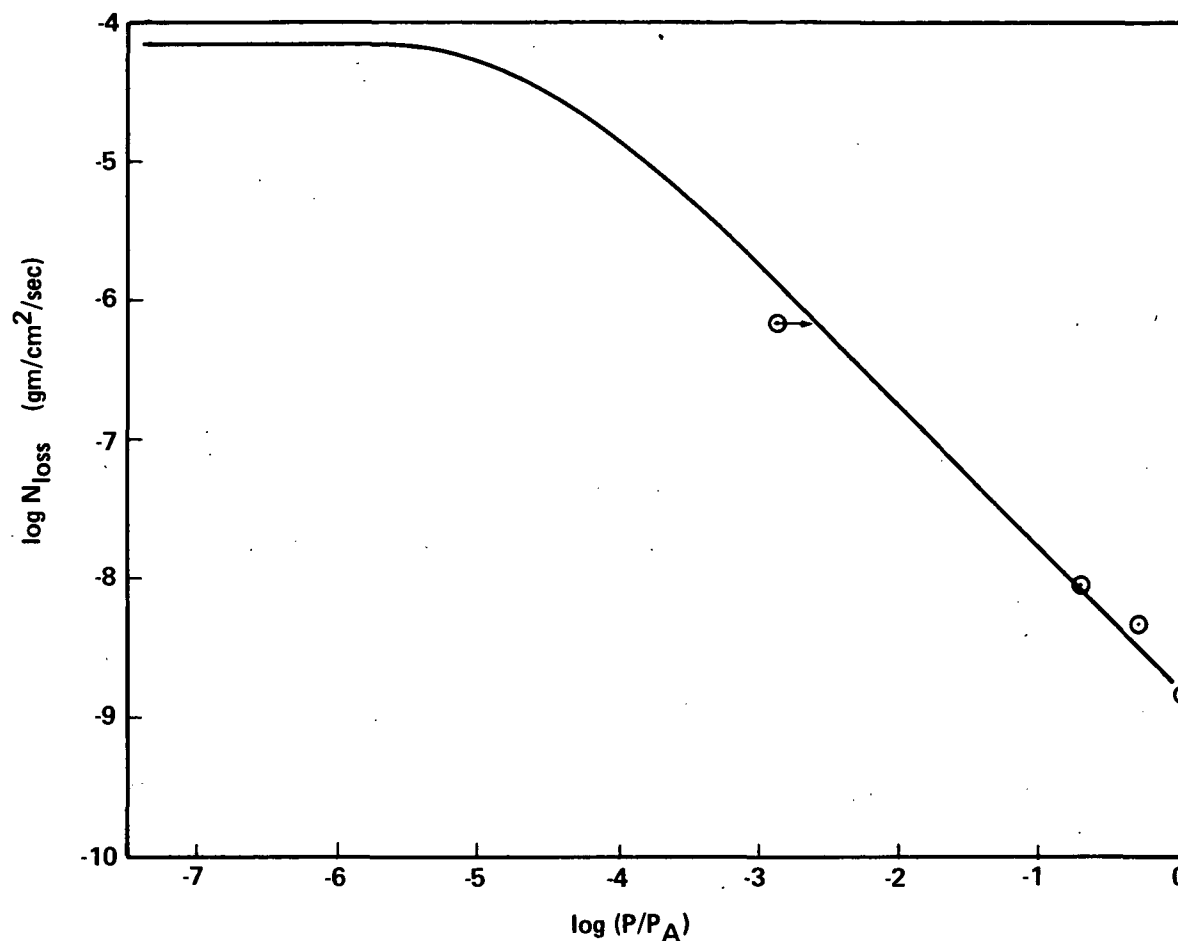


Figure 5. Theoretical evaporation rates (solid line) compared with observed evaporation rates (open circles) at various pressures.

(The point corresponding to 1 mm is a lower limit since the sample evaporated before this pressure was reached.)

The vapor pressure data of resorcinol can be estimated by [3]

$$\log P(\text{Torr}) = 9.7053 - \frac{3701.6}{T(^{\circ}\text{K})} \quad (24)$$

At 25 °C, $P = .0019$ Torr or 2.56 dynes/cm². \dot{N}_{evap} can be expressed in terms of mass loss by multiplying both sides of equation (23) by the molecular mass:

$$\dot{m}_{\text{evap}} = P_{\text{vap}} \sqrt{\frac{m}{2 \pi k T}} = 6.81 \times 10^{-5} \text{ gm/cm}^2/\text{sec} \quad (25)$$

The mean free path is given by

$$\lambda = \frac{k T}{\sqrt{2} \pi P (r_1 + r_2)^2} \quad (26)$$

where r_1 and r_2 are the radii of the ambient air molecules and the evaporated molecules, respectively. The effective diameter of an air molecule is taken to be 1.875 \AA . Since resorcinol has an atomic weight of 110, it is assumed to be $(110/28)^{\frac{1}{3}}$ larger. At $T = 298 \text{ }^\circ\text{K}$,

$$\lambda = \frac{4.13 \times 10^{-6}}{(P/P_{\text{atm}})} \text{ cm} \quad (27)$$

The dimension r_0 is essentially the range of the molecules before they are lost to diffusion. This was taken in the experimental case to be the radius of the sensing crystal, since any molecule diffusing beyond this range will no longer be counted. This is $r_0 = 0.25 \text{ cm}$.

Equation (20) for the experiment described becomes

$$m_{\text{loss}} = \frac{6.81 \times 10^{-5}}{2(.25) (P/P_{\text{atm}})} \quad (\text{gm/cm}^2/\text{sec}) \quad (28)$$

$$1 + \frac{\pi (4.13 \times 10^{-6})}{\pi (4.13 \times 10^{-6})}$$

This result is shown in Figure 5 for comparison.

CONCLUSIONS

The experiment demonstrated the fact that the model gives good results for the mass loss as a function of ambient pressure. It may be seen that materials whose dimensions are on the order of centimeters will lose mass a million times faster in a hard vacuum than at atmospheric pressure. Also, it may be seen that reducing the pressure below the point where the mean free path is of the same order as the sample dimension (10^{-3} Torr for centimeter-size samples) will not result in significant increase in mass loss.

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APPROVAL

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The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

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